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Electrochemical Formation of Au Clusters in Polyaniline

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The reduction of chloroaurate and the incorporation of Au clusters in polyaniline, PANI, films have been investigated. The chloroaurate complex is generated at the electrode surface during Cl^- doping of Au/PANI. FTIR and UV/vis data indicate that chloroaurate interacts with PANI and that its reduction to metallic Au occurs preferentially at the nitrogen linkages. The voltammetric and XPS results show that the uptake of both protons and anions is suppressed by the formation of Au clusters due to this interaction. The ability to reduce chloroaurate in PANI films is also demonstrated for Pt electrodes coated with PANI in solutions containing $KAuCl_4$. The preliminary results indicate that Au cluster size distribution remains fairly constant regardless of the method used.

Introduction

The extraction of metal anions into polyaniline, PANI, from aqueous solutions has been reported and suggested as a possible method of gold winning.[1] It is based on high affinity of metal anions for polyaniline and, in the case of chloroaurate anion, the spontaneous reduction of the PANI/aurate complex to metal at the open cell potential. It has been shown that the amount of accumulated gold may be as much as 5 times the original weight of the polymer.[2]

Composites of metal clusters and conducting polymers are useful for several applications. Incorporation of metal clusters is known to enhance conductivity of the polymer.[1c] Use of these composites as novel catalysts has also been suggested.[3] Finally, the incorporation of metal clusters allows metal−ligand interactions to be explored. We are interested in using metal clusters in conducting polymers as specific binding sites in chemical sensors.[4]

In the course of our systematic investigation of PANI as the matrix for chemical sensing layers, we have observed an anomalous behavior for thick (2−5 μm) layers of PANI deposited on gold electrodes in the presence of chloride ions. The studies indicated that the formation of chloroaurate and incorporation of gold in PANI takes place at the expense of the gold substrate. In other words, the gold electrode was actively corroded by chloride in the presence of PANI. This observation is interesting in itself because PANI has been recommended as the protective layer for variety of metals,[5] and growth of PANI from 2 M HCl has been reported.[6] In this paper we describe the systematic formation and reduction of chloroaurate at Au electrode covered with PANI.

Experimental Section

Chemicals. Tetrafluoroboric acid (Aldrich, 44wt % solution in water, 20,793-4), hydrochloric acid (J.T. Baker, 35.5−38 wt % solution in water, 9535-01), $KAuCl_4$ (Aldrich, 99.999% 45,023-5), and NaCl (Fisher) were all used as received.

Preparation of PANI−Formate Solution and Films. The bulk PANI was produced by oxidative electropolymerization of 0.25 M aniline in the presence of 2 M HBF_4. It was converted into PANI base with ammonium hydroxide.[7] A 250 mg sample of dry material was then dissolved in 50 mL of 88% formic acid. The PANI−formic acid solution was then filtered using 0.2 μm pore size syringe tip filters (Gelman Science, Acrodisk). PANI electrodes were cast onto Pt and Au electrodes using glass capillary pipets to minimize material overlap on the insulating body material of the microelectrodes. The volumes delivered onto the Pt or Au disk with a surface area of 0.14 cm^2 (model MF-2014 or MF-2013, Bioanalytical Systems) were on the order of 5 μL. The film thickness for these electrodes was typically between 2 and 4 μm. The formic acid was then allowed to evaporate from the PANI electrodes under normal laboratory air for 24 h before their further use as working electrodes in all electrochemical experiments.

Electrochemical Experiments. All electrochemical measurements were performed using CH Instruments model

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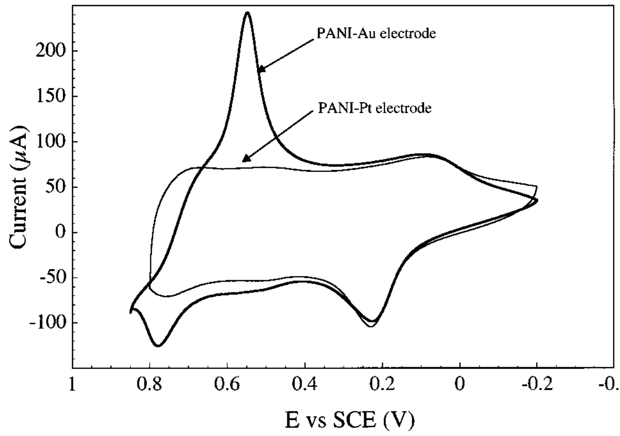

Figure 1. Steady-state cyclic voltammograms of Au/PANI and Pt/PANI electrodes immersed in 2 M HCl. Electrode area = 0.17 cm^2 and $\nu = 50$ mV/s.

CH1660 and CH1680 potentiostat/galvanostats connected in series and controlled by the electrochemical software. The experiments were made in a one-compartment cell. The potential of the working electrode was always measured against the saturated calomel electrode (SCE) using a double junction of 2 M acid. The counter electrode was a platinum foil. The width of the potential window used for each experiment was selected such that the voltammetric peaks corresponding to the proton and anion doping were fully developed. All cyclic voltammograms were recorded with a scan rate of 50 mV/s.

FT-IR Spectroscopy Apparatus and Conditions. FT-IR measurements were performed using a BIO-RAD FTS-6000 with a BIO-RAD UMA-500 IR microscope attachment. IR reflectance spectra were obtained using the rapid scan mode at a mirror modulation frequency of 20 kHz, with the aperture open, a filter setting of 5, a resolution setting of 4 cm^{-1}, and a laser wavelength of 15 800.8235 cm^{-1}. An average of 100 scans was used to produce each spectrum. Background spectra were obtained using a mirrored gold surface under the same spectroscopic conditions as the samples. The background was subtracted from the sample spectra using BIO-RAD WIN-IR PRO software. Areas and peak assignments were obtained using the same software.

XPS Apparatus and Conditions. XPS data were collected on a Phi Quantum 2000 scanning ESCA microprobe. This system uses a focused, monochromatic, Al Kα X-ray source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. The 100 μm diameter X-ray beam used had 100 W power and was rastered over a 1.5 mm by 0.2 mm rectangle on the sample. The X-ray beam was incident normal to the sample, and the X-ray detector was at 45° away from the normal. The multiplex scans were collected using a pass energy of 23.5 eV. For example, a sample containing Ag produces a Ag 3d$_{5/2}$ peak with a fwhm of better than 0.63 eV. All aliphatic carbon 1s peaks were assigned a binding energy of 284.8 eV to correct for the energy shift resulting from specimen charge neutralization. The PANI films cast on gold specimen were removed with a "Scotch tape" from the gold electrode prior to data acquisition. Finally, the core level spectra of the Au 4f peaks were charge shifted by 0.6 V in reference to the C 1s peak at 284.8 eV.

Results and Discussion

Electrochemistry. The voltammetric response of PANI films deposited on Au and Pt disk electrodes in 2 M HCl is presented in Figure 1. The doping mechanism for these films has been described in detail previously.[7] It is important to note that the cyclic voltammograms (CV) for PANI should not depend on the substrate on which it is deposited. This fact holds for all tested acids except HCl.[8] The CV for PANI deposited on gold is clearly different than that observed for PANI deposited on platinum. The PANI on Pt electrode shows the two characteristic doping regions corresponding to the uptake and expulsion of protons and anions in the acid solution. Although less well defined, these two doping processes can also be seen at the Au electrode. The proton doping (at ~0.1 V) is similar for the two electrodes, but the chloride doping at the Au/PANI electrode is significantly different. The uptake of anion occurs at nearly the same potential for both electrodes. On the other hand, a new cathodic peak at 0.57 V appears in the case of the Au electrode coated with PANI. This peak corresponds to the reduction of chloroaurate anion that was formed during the oxidation of the polymer at +0.80 V (Figure 1). The source of the Au^{3+} can only be the electrode itself. As the chloride ion enters the polymer, it penetrates through the 2 μm thick PANI film, reaching the electrode surface forming $AuCl_4^-$.[9] The chloroaurate anion forms a complex with PANI at the nitrogen linkage.[1] The negatively charged chloroaurate complex helps to maintain charge neutrality within the PANI phase as it is oxidized, but most of the negative charge is due to the BF_4^- anion. On the reverse scan, the chloroaurate complex is reduced to form metallic Au clusters in the PANI film. The steady-state voltammetric response indicates that the amount of Au that can form is dependent on the amount of chloride that diffuses into the PANI film. Furthermore, the oxidation and reduction of Au during cyclic voltammetry indicates that the postulated corrosion inhibition of PANI is not sufficient in the presence of Cl$^-$. This means that the electrode surface actively participates in the electrochemical process despite the fact that the PANI is relatively thick.

The formation of chloroaurate in PANI was also studied as a function of concentration of Cl$^-$ in the electrolyte (Figure 2). The cyclic voltammogram of an Au/PANI electrode in 2 M HBF_4 is shown as the bold line in Figure 2. Each additional CV corresponds to the increasing chloride ion concentration (shown as a parameter) while holding the HBF_4 concentration constant. A well-defined "isosbestic point" is observed at ~0.6 V vs SCE, indicating the transition between the expulsion of BF_4^- (taking place ~0.67 V) and reduction of the chloroaurate (observed at 0.53 V). This isosbestic point indicates that the formation and reduction of the chloroaurate in PANI is a reversible process and that $AuCl_4^-$ remains in the polymer despite a large excess of BF_4^-. The overall reaction can be described by the following scheme in which the potentials indicate the approximate appearance of these reactions:

$$\mathrm{Au} + 4\mathrm{Cl}^- \rightleftharpoons \mathrm{AuCl_4}^- + 3\mathrm{e}^- \qquad E > 0.80\ \mathrm{V}$$

$$\mathrm{AuCl_4}^- + \mathrm{PANI}^+ \rightleftharpoons [\mathrm{AuCl_4}^-/\mathrm{PANI}^+] \qquad E > 0.65\ \mathrm{V}$$

$$[\mathrm{AuCl_4}^-/\mathrm{PANI}^+] + 3\mathrm{e}^- \rightleftharpoons \mathrm{Au(0)} + \mathrm{PANI}^+ + 4\mathrm{Cl}^- \qquad E_\mathrm{p} = 0.55\ \mathrm{V}$$

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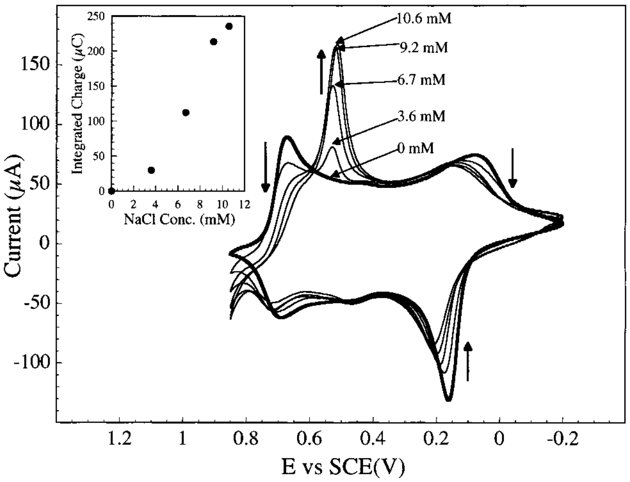

Figure 2. Cyclic voltammograms of a Au/PANI electrode immersed in a solution of 2 M HBF_4 recorded after consecutive additions of NaCl. Arrows indicate concentrations used and the trends of each voltammetric peak. Inset indicates the integrated charge under the peak as a function of the NaCl concentration. Electrode area = 0.17 cm^2 and $\nu = 50$ mV/s.

As the concentration of Cl^- increases, the anodic current associated with the formation of the chloroaurate complex and the reduction to Au(0) also increase. The inset in Figure 2 shows the charge under the reduction peak at 0.55 V as a function of the chloride ion concentration.

Considering the large excess of the BF_4^- anion, the uptake of Cl^- and formation of the chloroaurate are surprising. On the basis of concentration ratio alone, it would be expected that the anion uptake and expulsion would be dominated only by BF_4^-. The incorporation of chloroaurate results in the decrease of the peaks associated with the uptake (0.68 V) and expulsion (0.65 V) of BF_4^- similar to Figure 1. That indicates preferential and higher affinity of PANI for the chloroaurate complex. In addition, a decrease and a positive shift of ~50 mV of the voltammetric peaks associated with the uptake (~0.1 V) and expulsion (~0.2 V) of protons also indicates that PANI has a high affinity for the chloroaurate complex. The reduction of the proton doping peaks can only result if the nitrogen linkages in the polymer interact directly with the chloroaurate and Au clusters.

The dissolution of metal from the Au electrode in the presence of chloride is not an ideal procedure for producing polymer/metal composites. A better method involves the direct reduction of $KAuCl_4$ from solution to form Au clusters. Figure 3 shows the CV of PANI deposited on a Pt electrode immersed in a solution containing 2 M HBF_4 and 50 mM $KAuCl_4$. The reduction wave at 0.57 V vs SCE in the cyclic voltammetric response is consistent with the responses at 0.55 V shown in Figure 2. The proton uptake and expulsion peaks are again positively shifted. However, the voltammetric peaks associated with the uptake and expulsion of BF_4^- are clearly resolved.

The difference in the CV associated with the anion uptake and expulsion in Figures 2 and 3 can be attributed to the differences in the Cl^- concentrations in the electrolyte. In Figure 2, the highest concentration of free Cl^- in the electrolyte is 10.6 mM. The uptake and retention of the chloride occur because there is a higher concentration of the ion in the contact solution than in the PANI film which results in a concentration gradient. The accumulation of Cl^- requires that less BF_4^- uptake occurs to balance the charge in the PANI film. In contrast, there is little free chloride in the 50 mM $KAuCl_4$ electrolyte (Figure 3). Any chloride generated during the reduction of the $AuCl_4^-$ in the PANI film is free to diffuse out of the PANI film to the solution, where the Cl^- concentration is zero. In the case of the $AuCl_4^-$ solution, both anions are incorporated but BF_4^- continues to function as the dominant dopant anion. However, the expulsion of these two anions occurs in two separate steps: expulsion of BF_4^- at +0.80 V followed by reduction of more strongly bound $AuCl_4^-$ to Au(0) at 0.55 V.

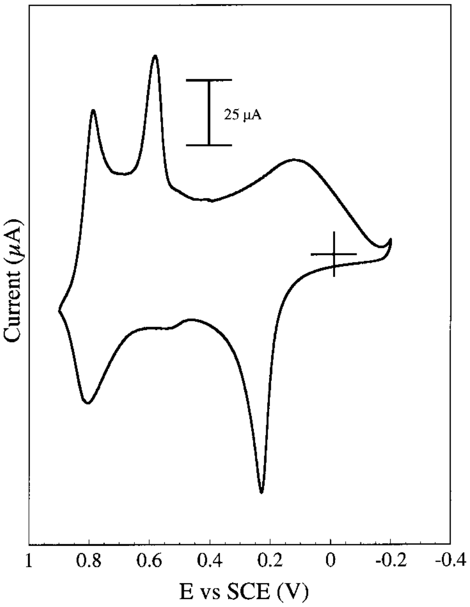

Figure 3. Steady-state cyclic voltammogram of a Pt/PANI electrode immersed in a solution of 2 M HBF_4 and 50 mM $KAuCl_4$. Electrode area = 0.17 cm^2 and $\nu = 50$ mV/s.

Figure 4 displays two microscopic images of PANI samples containing Au clusters. Figure 4 a shows PANI/Au-cluster composite resulting from dissolution of Au from the electrode and Figure 4b the PANI/Au-cluster composite obtained by reduction of $AuCl_4^-$ from solution at platinum electrode coated with PANI. The white spots in the images correspond to the Au clusters, and the black background is the PANI layer. The histograms extracted from these images indicate the size distribution of the Au clusters, calculated from the area of the a circular patterns in the image. For each sample a total of 10 voltammetric scans were performed. The histograms for the two samples indicate that 75% of the clusters for each sample fall between 0.10 and 0.40 μm^2. This area range represents clusters with diameters between 0.4 and 0.7 μm. Therefore, under similar voltammetric conditions the two procedures produce clusters with comparable size distributions.

Photoelectron Spectroscopy. XPS measurements were made to confirm that the formation and reduction of chloroaurate occur at 0.55 V. For this purpose, PANI films cast on gold substrates were cycled in solutions containing 1 M HCl and 1 M HBF_4 until a steady-state cyclic voltammogram was obtained. The film by nature of the voltammetric cycling was assumed to contain

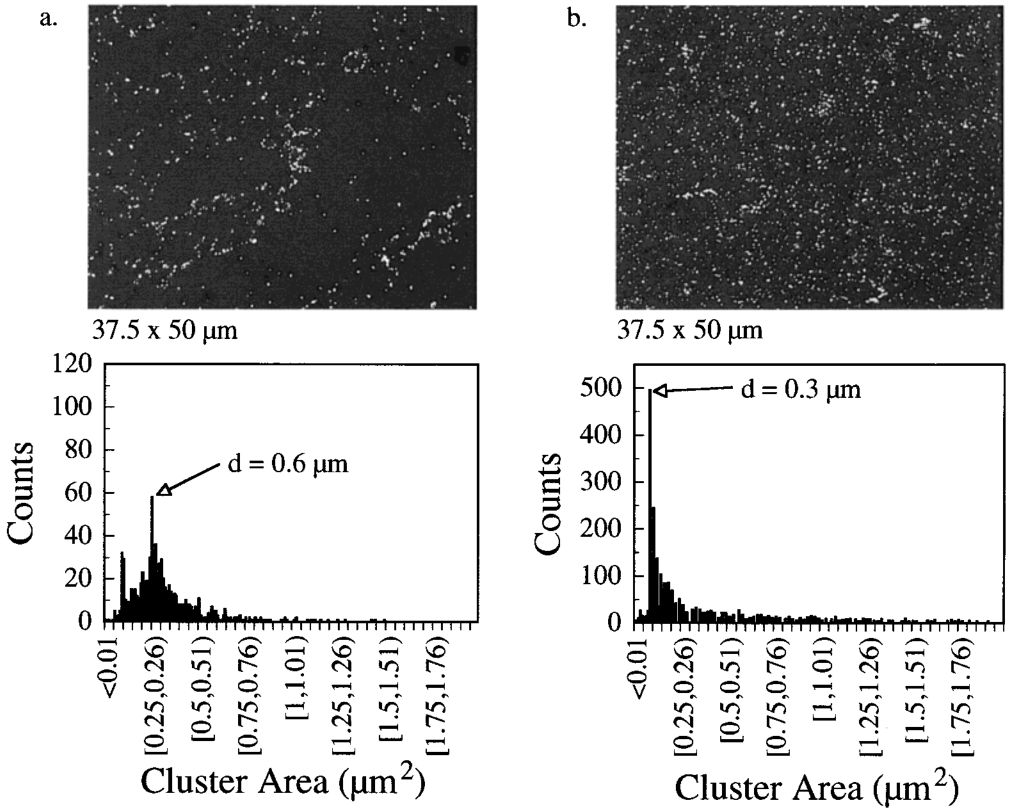

Figure 4. Optical micrographs of gold clusters on (a) Au/PANI from 10.6 mM NaCl in 2 M HBF_4 and (b) Pt/PANI from 50 mM $KAuCl_4$ in 2 M HBF_4. Corresponding histograms for each sample showing the cluster area and diameter for the largest peak are below each image.

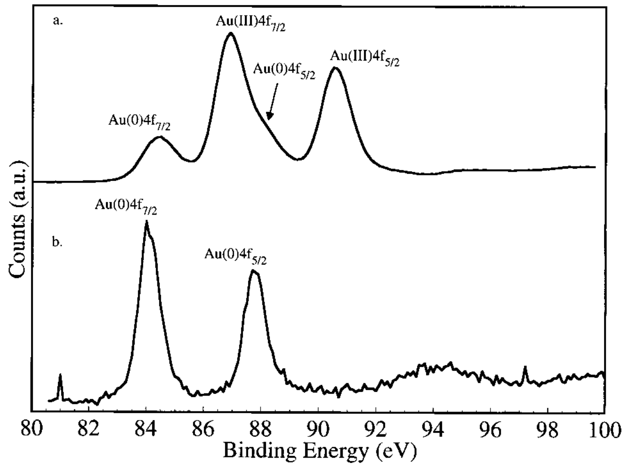

Figure 5. XPS spectra of (a) Au 4f taken from $KAuCl_4$ salt and (b) Au/PANI film cycled in a solution of 1 M HBF_4 and 1 M HCl. The corresponding peaks are labeled for clarity.

metallic Au at this point. The last scan of the cyclic voltammogram was stopped at 0.65 V before the reduction of chloroaurate. After that the sample was taken out of the electrolyte and briefly washed in deionized water. Gold clusters could be clearly seen under a microscope. The goal was to determine whether any chloroaurate remained in the PANI film without being reduced to metallic Au.

In Figure 5, the Au 4f core-level spectrum of PANI film containing gold clusters is compared with that of Au salt. Two strong peaks corresponding to the Au $4f_{7/2}$ and Au $4f_{5/2}$ lines indicate the presence of Au(0) species in both samples. Both absolute binding energies are located at 84 eV with a peak separation of 3.65 eV. The peak separation is consistent with the Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks.[10] More importantly, only metallic gold is present in the XPS spectra. The absence of gold species at higher oxidation states was proven by recording Au 4f core-level spectra of $KAuCl_4$ salt. In this spectrum, the Au^{3+} state corresponding to the $4f_{5/2}$ state was identified at 90.8 eV and the $4f_{7/2}$ at 87.2 eV. Therefore, we suspect that gold is present in the film exclusively as metal. The absence of higher oxidation states of gold agrees with previous observations made when oxidized PANI was allowed to relax in solutions containing chloroaurate.[2] The spontaneous and sustained reduction of chloroaurate anions by oxidized PANI resulted in an accumulation of elemental gold in the polymer.

In Figure 6 the XPS surveys of PANI, with and without Au clusters, are compared. The presence of BF_4^- anion in the film is confirmed in both spectra by F 1s and of B 1s lines. However, the intensity of F 1s and of B 1s peaks is significantly decreased, and new peaks of Au and Cl are observed after the reduction of Au into the polymer. The decrease in intensity of F 1s and of B 1s confirms that BF_4^- anion is replaced by chloroaurate in the PANI matrix during oxidation. The remaining chloride in the PANI matrix is likely due to the adsorption of Cl on the Au clusters.

Infrared and UV–vis Spectroscopy. Although the electrochemical and XPS data provide information about the mechanism for the gold cluster formation in PANI

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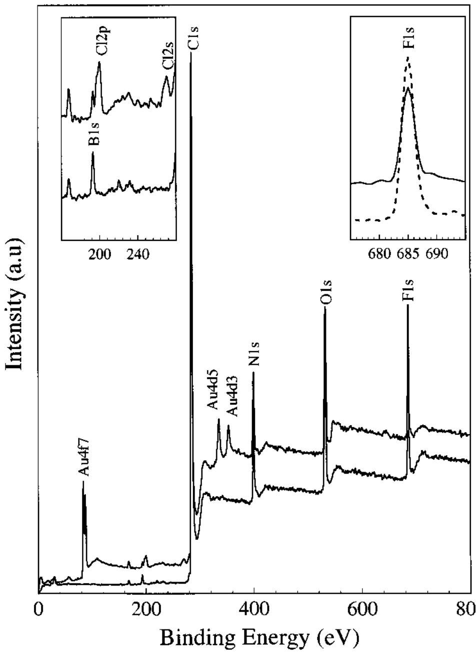


Figure 6. XPS surveys of Au/PANI films after cycling in 2 M HBF_4 (lower survey) and in 1 M HCl and 1 M HBF_4. Both electrodes were poised at 0.65 V before removing from the contacting solution. Insets show expanded regions for clarity.

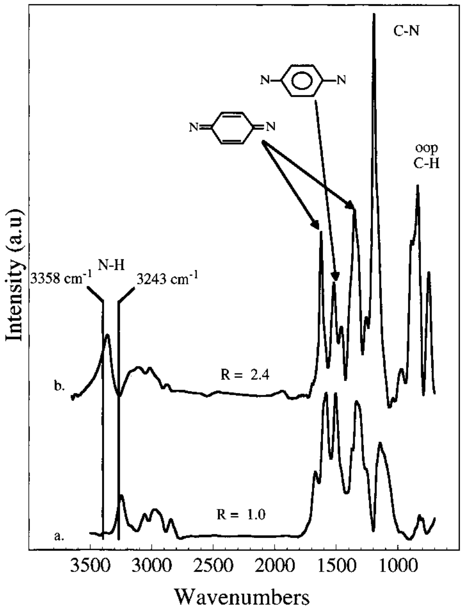
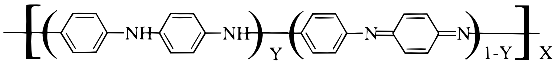


Figure 7. Reflectance FTIR spectra of (a) Au/PANI film before electrochemistry and (b) after cycling in 1 M HCl and 1 M HBF_4. The FTIR bands are labeled for clarity. The ratio, *R*, values are indicated above each spectrum.

films, the results do not contain sufficient information regarding the effect of Au clusters on the structure of the polymer. The affinity of the nitrogen linkages in the PANI film can be examined with reflectance FTIR spectroscopy to determine structural changes in the film after Au cluster incorporation. The reflectance IR spectra shown in Figure 7 highlight the difference between a PANI film before Au reduction (a) and a PANI film after Au reduction (b).

The electrochemical data indicate that the chloroaurate complex is reduced to metallic gold as the polymer is reduced. Furthermore, the formation of Au clusters must result in the withdrawal of electron density from the polymer (depletion of benzenoid units) due to the formation of quinoid units. The IR bands associated with the benzenoid and quinoid structures are shown in Figure 7. It was shown before that the oxidation state of PANI can be directly related to the aromatic C−C bands associated with the quinoid and benzenoid structures.[8b] The structure of PANI is generally represented by the following diagram, where $Y = 0.5$ for the polyemeraldine salt:[11]



The oxidation state of the polymer is characterized by the ratio $R = (1 - Y)/Y$ which is obtained from the ratio of intensities of the peaks at 1590 cm^{-1} (quinoid) and 1500 cm^{-1} (benzoid) bands.[12] The *R* values calculated from Figure 7 are 1.0 and 2.4 for the PANI film (a) and PANI film with Au clusters (b), respectively. The values indicate that the reduction of chloroaurate results in PANI films with more oxidized units. The data support the hypothesis that PANI acts a “wire”, transferring electrons to the chloroaurate to form metallic gold.

Additional information can be obtained from the vibrational N−H stretching region. The N−H stretch for PANI before Au reduction is located at 3243 cm^{-1}. However, the stretching frequency shifts to higher wavenumbers (~115 cm^{-1}) when Au is incorporated into the polymer. That indicates the withdrawal of electron density from the aromatic units,[13] causing significant structural reorganization in the polymer matrix. The structural change results also in the shift to higher wavenumbers for the bands associated with the aromatic C−C (benzenoid), C=N, C=C (quinoid), and “out-of-plane” C−H located at 1582, 1506, 1336, 1144, and 823 cm^{-1} for PANI and 1619, 1516, 1338, 1189, and 835 cm^{-1} for PANI with Au clusters.[12]

Finally, significant differences in the band shapes exist between the PANI film with and without Au clusters. The intensity of the bands in the fingerprint region is larger for the PANI film containing Au clusters. A rather significant change in intensity is observed for the out-of-plane C−H stretch at ~820 cm^{-1}, when Au clusters are present in the polymer. It has been suggested that this enhancement is caused primarily by surface enhancement infrared absorption effect which will be subject of a further study.[14]

It is important to note that reflectance IR spectroscopy is an ex-situ technique which does not allow the mechanism or structure of polymer to be probed during

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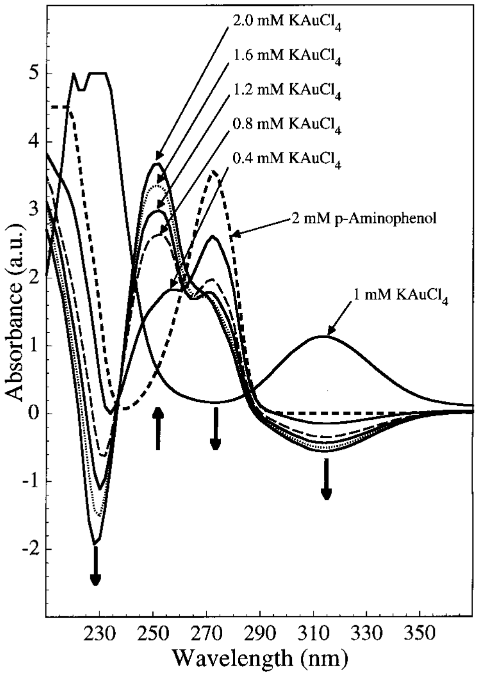

Figure 8. UV−vis spectra of 2 mM *p*-aminophenol with successive additions of $KAuCl_4$. Spectra of solutions containing only *p*-aminophenol and $KAuCl_4$ are also labeled. Each addition of $KAuCl_4$ represents an increase in concentration of ~0.4 mM as indicated by the arrows. Bold arrows under each absorbance peak indicate the direction of the intensity change.

the reaction. To pinpoint the nucleation centers involved in the formation of Au clusters, the surrogate reaction of *p*-aminophenol and $AuCl_4^-$ was examined using solution UV−vis spectroscopy. We have previously stated that the reduction of Au occurs at the nitrogen linkages in the polymer. If this is true, the oxidation of *p*-aminophenol should result in the formation of the quinone species. The reaction can be expressed as follows:

$$2AuCl_4^- + 3NH_2C_6H_4OH \rightleftharpoons Au(0) + 3NHC_6H_4O + 6H^+ + 8Cl^-$$

Figure 8 shows a series of UV−vis spectra for the reaction in solution containing 2 mM *p*-aminophenol and different concentrations of $KAuCl_4$. The spectra were obtained after addition of $KAuCl_4$ to both the reference cell and the cell containing *p*-aminophenol. Each successive addition results in an increase in $KAuCl_4$ concentration by 0.4 mM. A single absorbance band is observed at 274 nm for *p*-aminophenol before the addition of $KAuCl_4$ to the solution. However, with each successive addition of $KAuCl_4$ this band decreases in intensity. The consumption of $KAuCl_4$ is clearly observed at ~230 and ~313 nm. The transition between the bands located at 274 nm (*p*-aminophenol) and 250 nm (*p*-iminoquinone) is due to the spontaneous reduction of chloroaurate. The appearance of the band at 250 nm is consistent with the withdrawal of electron density from *p*-aminophenol.[12] The changes of the intensity are indicated with arrows in Figure 8. The UV−vis data confirm that the reduction of the chloroaurate occurs at nitrogen linkages.

Conclusions

The effect of small amount of Cl^- on the electrochemistry of the PANI/Au system is interesting in itself. It clearly shows that the electrolyte penetrates through relatively thick PANI layer and that the metal substrate participates in the overall electrochemistry. In other words, the electrochemical interface is not located at the macroscopic PANI/electrolyte boundary but must be formulated in terms of the “PANI bulk” *and* the metal substrate. The participation of the metal substrate is not evident for electrolytes that are not electroactive within the applied potential window, such as HBF_4, H_2SO_4, etc.

The uniform distribution of gold clusters within the bulk of PANI can be explained in terms of the chloroaurate/aminophenol redox equilibrium shown in Figure 8. The imino groups within PANI have a high affinity for chloroaurate. On negative sweep of potential, at approximately 0.5 V, PANI chains conduct electrons to the $AuCl_4^-$ which is reduced to Au(0). Upon reoxidation of the PANI, $AuCl_4^-$ is again formed, thus freeing up the imine site for further interactions. Cycling of this system therefore produces Au clusters located in the vicinity of the imine sites. During this process Cl^- does not leave the PANI layer but shuttles from the $AuCl_4^-$ to the metal clusters, forming $Au(0)/Cl^-_{ads}$. The required charge neutrality within the polymer phase is maintained by the decreased amount of BF_4^- as evident from the XPS data (Figure 5). In addition, the presence of Au clusters in PANI is apparently responsible for a dramatic increase in intensity of IR bands based on the surface-enhanced IR effect.[15]

The preferential interaction of chloroaurate at nitrogen linkages also affects the proton uptake, decreasing and shifting the protonation peaks in Figure 2. The cyclic voltammograms recorded at PANI/Pt electrode in 50 mM chloroaurate solution show that most imine sites are occupied, resulting in the distortion of the proton exchange (Figure 3). Again this mechanism is corroborated by the FTIR spectrum (Figure 7). The polyaniline acts as a three-dimensional, random, and electronically conducting template that allows formation of relatively uniform gold clusters. The optimization of the conditions for the controlled growth of metal clusters in PANI is in progress.

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